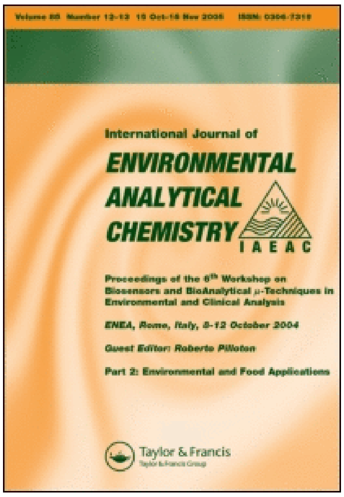

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QUANTITATIVE ESTIMATION OF CONSTITUENTS IN FLY ASH BY LITHIUM TETRABORATE FUSION

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Silica is removed from fly ash sample by hydroflourination for its effective determination gravimetrically and the remaining residue is subjected to lithium tetraborate ($Li_2B_4O_7$) fusion followed by dissolution in dilute nitric acid to obtain a clear solution in which elements including aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu) and zinc (Zn), have been determined by Flame Atomic Absorption Spectrometry (FAAS). Two fly ash samples analyzed by the proposed method have been received from the National Council of Cement and Building Materials (NCCBM), India (proposed CRM in future) and fly ash CRM 1633 (b) from NIST, USA. The validity of the method has been established by analyzing fly ash CRM 1633 (b) as reference standard. The standard deviation has been calculated for each measurement.

Keywords: Fly ash; Hydrofluorination; Lithium tetraborate ($Li_2B_4O_7$) fusion; FAAS

INTRODUCTION

The role of fly ash in environmental pollution causes high concern in India. The accurate compositional analysis of fly ash has been of primary importance to analytical scientists over the years. Method used for the decomposition of silicates for chemical analyses are usually based on the use of acids or fluxes like sodium carbonate, fusion mixture etc. Bernas [1] and Langmyhr and Paus [2] have used a mixture of hydrofluoric acid with other acids to prepare silicate solutions using special Teflon equipment. Alkali fusion has been widely adopted for the analysis of major constituents such as silica, alumina and titanium and acid dissolution for iron, calcium, alkali metals etc. However, this approach involves complex dissolution techniques and though practicable is not suitable for routine analysis. Ingamells [3] and Owens and Ernest [4] have given emphasis to the use of lithium metaborate, which has the advantage of brining the sample into solution in one single fusion, as lithium and boron are rarely

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encountered in fly ash materials. Van Loon and Parissis [5] and Iwata *et al.* [6] have given good accounts of silicate analysis by lithium metaborate fusion followed by FAAS analyses. ASTM [7] has also brought out a standard test method for major and minor elements in coal and coke ash based on FAAS using lithium tetraborate. Foder [8] used a hydrofluoric and boric acid mixture for the determination of silica in fly ash. Csondes *et al.* [9], Betlinelli *et al.* [10], Brunori *et al.* [11] and Polyak and Halvay [12] have done a comparison study of fly ash samples by different methods. Torigai *et al.* [13] have determined several elements in fly ash by microwave digestion using $HClO_4/HNO_3/HF$. Swami *et al.* [14] have used microwave digestion using HNO_3/H_2O_2 for the determination of trace elements in fly ash by ICP-AES. Das *et al.* [15] have also used a microwave digestion technique for the analysis of several elements in fly ash using ICP-MS. In the present investigation hydrofluoric acid is used to decompose the fly ash present as silicates and subsequently determine silica quantitatively. The remaining residue has been fused with lithium tetraborate, and subsequent dissolution in dilute nitric acid gives a clear solution. In the solution, Al, Fe, Mg, Na, K, Ti, V, Cr, Mn, Ni, Cu, Zn have been determined by FAAS. The accuracy of the method has been compared by analyzing fly ash CRM 1633 (b) from NIST and comparing the values with certified values [16]. A comparative measurement of the NCCBM fly ash sample using the ASTM method has also been done.

EXPERIMENTAL

Apparatus

Details of equipment and standard setting for FAAS measurement are given in Table I Calibrated pipettes and volumetric flasks from Borosil Glass Works Ltd. India were used. A magnetic stirrer ST-150 with heater was used (Toshniwal India Limited) with a Teflon-coated magnetic stirring bead. Platinum dishes of 99.99% purity obtained from Arora Matthey (Kolkata) India were used, and were cleaned by potassium hydrogen sulphate fusion before each experiment. All the digestion processes were carried out

TABLE I Details of instrument and standard setting for FASS measurements

		Varian spectrAA-10 atomic absorption spectrophotometer[a]		
Element	*Detection limit*[b] (mg/L)	*Wavelength* (nm)	*Slit width* (nm)	*Flame conditions* (L/min)
Iron	0.003	248.3	0.20	Air/acetylene 5.0/0.8–1.0
Aluminum	0.04	309.3	0.50	Nitrous oxide/acetylene, fuel rich 5.0/4.5–5.0
Titanium	0.12	364.3	0.50	Nitrous oxide/acetylene, fuel rich 5.0/4.5–5.0
Calcium	0.001	422.7	0.50	Air/acetylene 5.0/0.9–1.1
Magnesium	0.0002	285.2	0.50	Air/acetylene 5.0/0.9–1.1
Potassium	0.003	766.5	1.0	Air/acetylene 5.0/0.8–1.0
Manganese	0.003	279.5	0.20	Air/acetylene 5.0/0.8–1.0
Sodium	0.0002	589.0	0.50	Air/acetylene 5.0/0.8–1.1
Chromium	0.003	357.9	0.20	Air/acetylene 5.0/1.0–1.2
Zinc	0.0026	213.9	1.0	Air/acetylene 5.0/0.8–1.1
Nickel	0.007	232.0	0.20	Air/acetylene 5.0/0.8–1.0
Copper	0.004	324.8	0.50	Air/acetylene 5.0/0.15–0.20
Vanadium	0.05	318.5	0.20	Nitrous oxide/acetylene Fuel rich 5.0/4.5–5.0

[a] Inbuilt spray chamber. Flame wavelength range: 190–900 nm; [b] Sample intake rate 5 mL/min.

in a cleaned laminar flow bench equipped with the appropriate ventilation system from Atlantis (India).

Reagents

Nitric acid (69%) and hydrochloric acid (35%) of GR grade (Guaranteed Reagent) were further purified by sub-boiling point distillation in a quartz glass apparatus. Sulphuric acid (98%) and potassium hydrogen sulphate GR grade, both from E. Merck (India), lithium tetraborate (98%) ($Li_2B_4O_7$) from E. Merck (Germany) and hydrofluoric acid (49%) of semiconductor grade (Fluka) were used. De-ionized water (18 MΩ resistivity) prepared using a Millipore milli-Q water purification system (USA) was used. Standard stock solutions of 1000 mg/L of all the elements were prepared from high-purity metals or salts (99.99%) in sub-boiled nitric acid or sub-boiled hydrochloric acid according to the ASTM procedure, made to the final volume with de-ionized water. Subsequent dilutions of the stock solutions were performed to get the desired concentration. These solutions were used for calibration of the instrument.

Procedure

TWO samples of fly ash, (1) received for testing from NCCBM and (2) CRM 1633 (b) fly ash from NIST, were taken as samples, dried at 110°C for 1–2 h Weighed samples (0.25 g) of each material (ten replicates) were transferred into weighed platinum dishes (volume 100 mL). Hydrofluoric acid (10 mL) was added followed by a few drops of sulphuric acid in each sample, which was heated over a hot plate with controlled temperature to decompose the fly ash present as silicate and volatilize silica as silicon tetrafluoride. Further hydrofluoric acid (10 mL) was added to each sample to complete the hydrofluorination. The complete removal of silica was judged by the change of color of the sample from gray to white.

The residue left in the platinum dish was heated to 1000°C for a few minutes to convert it to oxides and the process of heating, cooling and weighing was repeated until constant weigh was obtained, and the silica content was determined gravimetrically by this process. The remaining residue containing oxides of other elements was fused with an equal mass (1 : 1) of $Li_2B_4O_7$ at 1050°C for 15 min and cooled. The residue was dissolved in 1:1 HNO_3 (30 mL) and heated at 70–80°C with continuous stirring. The clear solution obtained was transferred to a 100 mL volumetric flask and made up to volume with de-ionized water.

The other elements present in fly ash, namely Al, Fe, Ca, Mg, Na, K, Ti, V, Cr, Mn, Ni, Cu and Zn, were measured in the solution by FAAS using the respective standard for each element during measurements. In the ASTM method the sample (0.1 g) was mixed with $Li_2B_4O_7$ (0.5 g) and additional $Li_2B_4O_7$ (0.5 g) was added to cover the mixture. After heating at 1000°C for 15 min the angle was dissolved in HCl (80 mL; HCl : water: 5 : 95) and the volume was made to 100 mL. A reagent blank was also prepared without the sample and a correction applied whenever required. The mean absorbance value of the ten replicates of each sample of NCCBM and NIST standard was used when calculating the concentration of each analyte element.

Calibration

The calibration of the instrument was carried out with standard solutions covering the desired concentration range of the analytes in the sample. The standard required for calibration of FAAS for different elements were prepared as mentioned in the ASTM procedure for coal and coke ash. Standard additions of A1 and Fe in the required proportions were added to the standards of transition elements of interest to match the sample solution to avoid the interference of A1 and Fe in their analysis. In the determination A1 and Fe also, the standards were matched according to the requirements of the sample. When standard solutions of Na, K, Ca and Mg were prepared, 1% lanthanum as lanthanum chloride solution was added as ionization buffer. During the measurements of Na, K, Ca and Mg in the standard sample, 1% lanthanum as lanthanum chloride was also added to each sample solution during dilution. For titanium, the standard solution was prepared in sub-boiled hydrochloric acid. $Li_2B_4O_7$ was added to all the standard as required.

RESULTS AND DISCUSSION

A new approach for sample dissolution has been adopted whereby a hydrofluorination process has been directly to remove silica from fly ash silicates completely and determine it quantitatively. This is an empirical method for silica determination, as the loss in weight during hydrofluorination is presumed to be purely due to silica. The further loss in weight may be due to the presence of some volatile elements like Hg and As, which are present at a milligram per liter level. The results obtained for silica determination is NIST fly ash CRM 1633 (b) by a conventional gravimetric method and the proposed method are $23.0 \pm 0.26\%$ and $22.99 \pm 0.10\%$ respectively, against the certified value $23.02 \pm 0.08\%$. The results obtained for fly ash (NCCBM) by a conventional gravimetric method and the proposed method are $28.00 \pm 0.17\%$ and $27.95 \pm 0.09\%$, respectively. As can be seen from the results, the values obtained for silica for the fly ash samples from NCCBM and NIST CRM 1633 (b) by both methods are reproducible, so the proposed method gives a reproducible result for silica present in the samples.

As silica, the major constituent of fly ash, is removed as SiF_4 the mass of lithium tetraborate used for fusion of the remaining residue is substantially reduced and is used in the ratio 1 : 1 with respect to the remaining sample weight. This is an advantage for FAAS determination of the remaining elements, as the salt concentration is considerably reduced, as is the blank. The solution obtained after fusion with $Li_2B_4O_7$ and subsequent dissolution in dilute HNO_3 remains clear without any development of turbidity, even after keeping it for several days. In the process given by ASTM the solution was turbid in most cases or turbidity appeared in the solution during cooling. For this reason the process needed to be repeated several times. In the microwave digestion process, although it takes less time for digestion and the method is best for volatile elements after digestion it takes 25–30 min to normalize the pressure of the vessel and if the process of digestion is repeated it takes more time for dissolution.

For the determination of silica after hydrofluorination, heating at 1000°C for conversion into oxides and fusion at 1050°C is not possible in the microwave digestion process. The results obtained by the FAAS method for major and minor elements are presented in Tables II and III, respectively, for the two samples. The results

TABLE II Major elements present in samples as mass percent

Element	*NIST Fly Ash 1633(b)*		*Fly ash (NCCBM)*	
	NIST certified value (±)[a]	*Proposed method value* (±)[b]	*Proposed method value* (±)[b]	*ASTM method value* (±)[b]
Aluminum	15.05 ± 0.27	15.14 ± 0.04	15.11 ± 0.06	15.20 ± 0.30
Iron	7.78 ± 0.23	7.63 ± 0.08	4.84 ± 0.08	4.80 ± 0.27
Calcium	1.51 ± 0.06	1.46 ± 0.03	1.20 ± 0.03	1.26 ± 0.10
Magnesium	0.482 ± 0.008	0.470 ± 0.06	0.310 ± 0.06	0.317 ± 0.08
Sodium	0.201 ± 0.003	0.195 ± 0.06	0.081 ± 0.007	0.085 ± 0.008
Titanium	0.791 ± 0.014	0.770 ± 0.02	1.06 ± 0.02	1.10 ± 0.02
Potassium	1.95 ± 0.03	1.92 ± 0.01	0.65 ± 0.02	0.71 ± 0.04

[a]Uncertainty of measurement as mentioned in certificate; [b]Standard deviation of ten replicates of each sample.

TABLE III Comparative result of minor elements by FAAS

Element	*NIST Fly ash 1633(b)* (mg/kg)		*Fly ash (NCCBM)* (mg/kg)	
	NIST certified value (±)[a]	*Proposed method value* (±)	*Proposed method value* (±)[b]	*ASTM method value* (±)[b]
Vanadium	295.7 ± 3.6	299.5 ± 3.0	175.3 ± 3.6	173.4 ± 4.0
Chromium	198.0 ± 4.7	196.0 ± 3.9	148.4 ± 5.1	145.4 ± 5.6
Manganese	131.8 ± 1.7	128.2 ± 1.2	690.1 ± 9.3	693.0 ± 8.8
Nickel	120.6 ± 1.8	117.3 ± 1.4	112.4 ± 2.4	113.4 ± 3.0
Copper	112.8 ± 2.6	1101.1 ± 2.1	100.2 ± 2.8	99.0 ± 3.3
Zinc	210[c]	206.0 ± 3.9	212.3 ± 3.9	211.0 ± 5.0

[a]Indicates uncertainty of measurement as mentioned in the certificate; [b] Standard deviation of ten replicates of each sample; [c]Indicative value.

obtained by the developed method for CRM 1633(b) of NIST have been compared with NIST certified values and the values obtained for fly ash sample of NCCBM are compared with the obtained following the ASTM method for coal and coke ash. The results obtained for the other elements determined by FAAS show excellent agreement between the certified values and the values obtained by the proposed method for fly ash CRM 1633(b) of NIST and also the fly ash sample of NCCBM. The reproducibility is found to be better for the proposed method, and the uncertainties are reported as standard deviations using ten replicates of each sample. Blank levels have been found to be very low for the elements reported. All the data reported have been corrected for the blank.

CONCLUSION

Results obtained for each element by the proposed method have been found to be reproducible for the accurate and precise determination of major and minor elements in fly ash.

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